

of catacondensed aromatics increase markedly as the bands approach one another. Furthermore the sign of the MCD appears to change in tetracene as the energies of L_a and L_b are interchanged. (Unfortunately solubility problems have thus far obviated measurements on pentacene where these bands are more clearly separated.) The inequality of the MCD for the interacting bands, which argues against this simplest two-level interpretation, could be the result of an accidental overlap of positive and negative bands.

The basis for the second conclusion is that in a series of catacondensed aromatics and simple substituted benzenes the sign of the MCD of a particular band is nearly always related to the direction of the transition moment for that band. Thus, in those catacondensed aromatics studied the MCD is always positive for bands with transversely directed transition moments, e.g., the L_a band in naphthalene. (In phenanthrene, where the polarization directions of the L_a and L_b bands are reversed, it was observed that the signs of the MCD are changed.) In simple substituted benzenes such as *o*-, *m*-, *p*-xylene, bromobenzene, phenol, and *m*-cresol

the L_b MCD bands are positive. However, in several instances in which $n \rightarrow \pi^*$ transitions were near the L_b band the sign appears to be reversed, e.g., benzaldehyde.

The most obvious application of this spectral method is for "labeling" electronic transitions in complex molecules. Thus, if our interpretation is correct, the negative band at 28 000 cm^{-1} in anthracene is the L_b band which was predicted at this energy.⁵ In another study presently under way in this laboratory it has been learned that the accidental degeneracies observed in several heterocyclics⁶ by the polarization of fluorescence can even more readily be observed by MCD. This method may also facilitate making symmetry assignments to electronic states.^{2,3} For example, when MCD spectra indicate that two electronic states mix strongly, the direct product of their irreducible representations must span one of the irreducible representations of the angular-momentum operator under the same point group.

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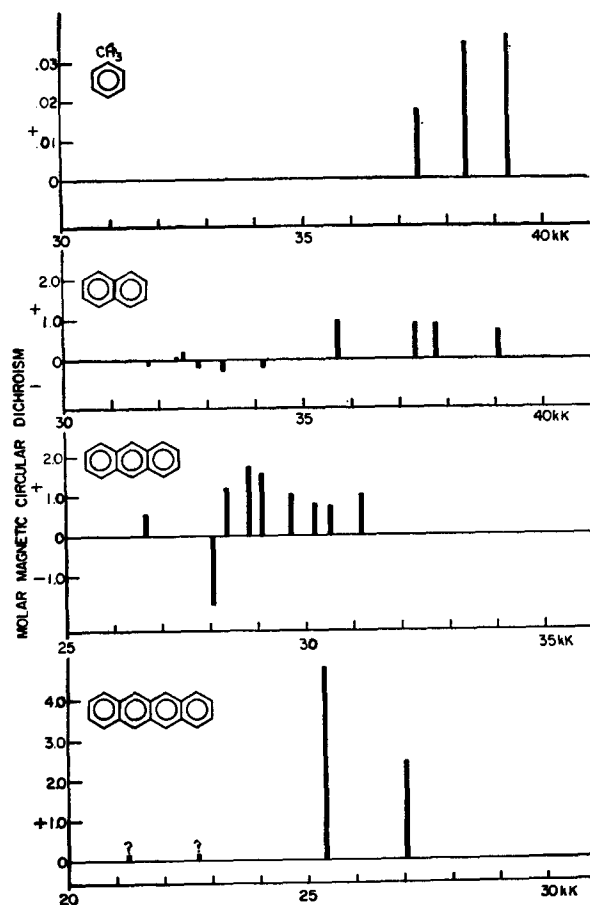


FIG. 1. Molar magnetic circular dichroism of toluene and several catacondensed aromatics. Note 100-fold ordinate expansion for toluene.

Field-Induced Quantum States at a Surface*

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IN an earlier Communication¹ we reported the presence of structure in energy distributions of ions produced in a high electric field near a metal surface. It was stated that the parent-ion energy distribution showed a main peak with high-energy onset corresponding to a minimum distance from the surface for ionization and an unexpected series of secondary peaks at lower energies, i.e., formed at greater distances from the surface. The suggestion offered that these peaks might be due to virtual surface states related to the crystal lattice has proved to be inadequate. The predicted variation in peak spacing with crystal orientation could not be experimentally demonstrated. We now propose an interpretation of the nature of the secondary peaks which involves resonances of the atomic levels with the levels of a one-dimensional triangular well formed by an electric field and the surface. In this model

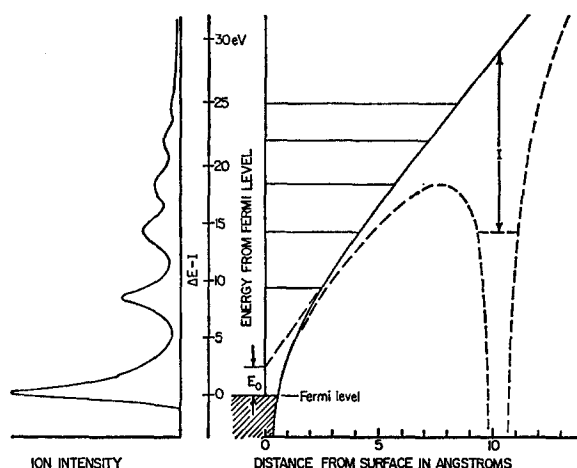


FIG. 1. Plot of surface-potential configuration on the right and observed ion energy distribution on the left for H_2 molecules with an applied field of approximately 2.5 V/\AA . The ion distribution is shifted from ΔE (the energy deficit from surface potential) by I , the ionization potential, so that the features are aligned with the pertinent level. The potential distribution with an atom (of $I = 15.6 \text{ eV}$) present is drawn in dashed lines. Extrapolation of the potential energy (not including the atomic field) to the surface defines E_0 . Locations of the first five stationary states of the infinite triangular well are also shown. The scale in the center is in electron volts and applies to both sides.

the surface states depend on the field rather than the crystal lattice.

The conventional model of a surface, with an atom near that surface, in an electric field is shown in Fig. 1. Low-energy electrons tunneling into the roughly triangular well outlined in the figure have a certain probability of being reflected by the metal surface.² That such reflectivity exists can be empirically demonstrated by the familiar difficulty of collecting low-energy electrons; special means such as a Faraday cage must be used for quantitative collection. If the reflectivity is unity and tunneling back to the atom is unlikely, well-defined energy levels will exist within the well. Lower reflectivities will result in short-lived states and consequent level broadening.

Alternately, the problem may be described in terms of the matching of wavefunctions at the boundaries of the three regions of interest: the atom, the triangular well, and the surface. The probability amplitudes in the region of linearly increasing potential are given in terms of Airy functions³ and are initially unspecified in amplitude and phase. These two parameters are fixed by equating logarithmic derivatives at the boundaries and result in small amplitudes in the well except at energies near the eigenvalues of the simple infinitely high triangular well. Consequently, low tunneling rates are expected for atomic levels not aligned with the well levels. The presence of the atomic potential and associated image force acts as a small perturbation on the well levels. A calculation using square potentials verifies this picture; a square well open on one side to a higher-energy continuum demonstrates resonances at energies very near to the closed-well eigenvalues.

Eigenvalues E_n of the infinite triangular well are given by the relation

$$-(2m/\hbar^2 e^2 F^2)^{1/3} E_n = a_n,$$

where m is the electronic mass, e the electronic charge, F the field, and a_n the n th root of the particular Airy function which is finite for all real values of its argument. To complete a rough correspondence with our picture, we must add to E_n a quantity E_0 given by the difference between the Fermi energy and the energy at which the extrapolated field curve intersects the surface. Results of this calculation and an observed distribution are compared in Fig. 1. Good agreement is not expected for the first level because of the influence of the image potential which is not included in the above calculation and because of the sensitivity of this level to the assumed surface configuration. The calculated variation of peak spacings with electric field agrees closely with experimental values and, over the energy range observable, is very nearly indistinguishable from a first-power field dependence.

In addition to the main structure explained above, the experiments show further detail in peak structures indicative of the nature of the surface and surface reactions. It is expected that this type of analysis will be useful in surface studies. For example, it is to be noted that a pure surface reaction such as H_3^+ formation exhibits no secondary structure.¹

The model described here is simplified and lacking in detail but is believed to be essentially correct. A more thorough analysis and presentation of data will be submitted at a later date.

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Energy Threshold for $D + H_2 \rightarrow DH + H$ Reaction*

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WE have been able to measure the threshold energy E_0 for the reaction $D + H_2 \rightarrow DH + H$. The value obtained was $(0.33 \pm 0.02) \text{ eV}$. Apparently, this is the first direct determination of a threshold energy for a reaction involving the formation and breaking of covalent bonds.

The method used consists of photolyzing a mixture of DI or DBr plus H_2 with monochromatic light and determining the wavelength dependence of the resulting